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The Comparison of Magnetite Nanospheres Formation in Polysaccharide Covers by Various Ways of Syntheses

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In this work the ways of magnetite nanoparticles formation in polymer covers were proposed. Polysaccharides solutions (alginate, chitosan) were used as biopolymers. Three ways of magnetite nanoparticles formation in polymer covers were proposed: 1) synthesis, where magnetite particles were coated with a polymer cover by using the gel-forming components applicable for appropriate polymers; 2) mixing of magnetite particles with the solution of an appropriate polymer (sodium alginate, chitosan); 3) spray method, where the mixture of a magnetic nanocomposite was sprayed by compressed air, while in two other ways an ultrasonic dispersion was used.

The following techniques were used for the analysis: transmission electron microscopy, electron and X-ray diffractions. The study of the structural features show that spray method and synthesis have the advantages over simple mixing, because the obtained particle size of 4-22 nm was less than 50-100 nm. It was shown that the use of alginate as polymer compound increases the crystallinity of magnetic nanocomposite, while the use of chitosan leads to magnetite lattice contraction and increase in its structure imperfection.

Keywords: Magnetic nanoparticles, Magnetic nanocomposites, Alginate, Chitosan, X-Ray Diffraction, Transmission electron microscopy, Electron Diffraction, Particle size.

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1. INTRODUCTION

A significant part of studies has been recently devoted to nanostructured magnetite due to the possibility of its application in medical practice for targeted drug delivery as well as for diagnostics and treatment because of hyperthermal action on tumor cells [1, 2].

Ways of synthesis of magnetite and iron oxides nanoparticles are of technological and scientific interest, since they influence both the physical and chemical properties of magnetite nanoparticles [3]. Sol-gel method [4], microemulsification [5], thermal decomposition [6], co-deposition [7] and reverse deposition [8] are among the main synthesis methods. Magnetic nanoparticles are inclined to agglomeration and oxidation in air; therefore, there appears a necessity to use polymers for their stabilization [8, 9]. Chitosan, which is a polysaccharide of natural origin, is efficiently used for stabilization of nanosized magnetite [10]. It was established that nanoparticles sizes significantly decrease during deposition of magnetite in chitosan matrix [11]. In this work, the studies were continued using polysaccharide matrices of sodium alginate, which is not expensive and non-toxic universal material [12, 13] and for which the thermal stability and a frequent use as a drug carrier including combinations with magnetite nanoparticles applied for immobilization of enzymes are typical. The main advantages of the use of sodium alginate are the following: ability to form hydrogels at pH and existence temperatures of living cells, proteins, enzymes and nucleic acids; strengthening of nucleation and growth of hydroxyapatite; anticoagulant properties like of heparin; strengthening of interaction between the cells and biomaterial surface; change in the hydrophobic-hydrophilic balance for the optimum drug yield and also ability to biodegradation [13]. In connection with the urgency of the use of natural polymers (sodium alginate and chitosan) [14-17] as a cover, there appears a necessity to seek the ways of introduction into them of magnetite nanoparticles. In the given work, we propose three methods for obtaining magnetite nanoparticles in a polymer cover, namely, synthesis, mechanical mixing and spray method; the comparison of the basic characteristics of the obtained materials has been performed.

2. MATERIALS AND METHODS

Synthesis of magnetite (Fe_3O_4) was performed by the chemical deposition method according to the following reaction equation:

$$2FeCl_3 \cdot 6H_2O + FeSO_4 \cdot 7H_2O + 8NH_3 \cdot H_2O \rightarrow Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 23H_2O.$$

This method includes co-deposition of Fe^{2+} and Fe^{3+} ions in the presence of NaOH or $NH_3 \cdot H_2O$ [18, 19] at relatively low temperatures of 80-85 °C.

5.41 g of $FeCl_3 \cdot 6H_2O$ and 3.058 g of $FeSO_4 \cdot 7H_2O$ were separately dissolved each in 50 ml of distilled water and then mixed; after that 40 ml of 25 % ammonia solution were added drop by drop into the mixture at the temperature of 80 °C to obtain pH not lower than 10.4. Sediment was left for a day for aging. Then, washing of the obtained highly dispersed uniform sediment of magnetite was performed to pH = 7.0 of the washing solution.

When carrying out the experiments on compound of polymers molecules with magnetite nanoparticles, the emphasis was done on the formation of spherical granules by polymers molecules during interaction with different gel-forming components, here magnetite remained chemically neutral.

1AS – Synthesis of nanospherical magnetite particles in alginate cover. 5 ml of 1 % aqueous solution of sodium alginate were mixed with 500 μl of magnetite suspension

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in distilled water, then the formed mixture was sprayed into 0.1 M $CaCl_2$ solution. Gelation with the formation of spherical granules with the magnetite particles inside occurs during interaction of sodium alginate with bivalent Ca^{2+} ions.

1XS – Synthesis of nanospherical magnetite particles in chitosan cover. 5 ml of 1 % aqueous solution of chitosan were mixed with 500 μl of magnetite suspension in distilled water, then the obtained mixture was sprayed into 0.1 M solution of sodium tripolyphosphate. During its interaction with chitosan macromolecules, gelatinous spherical granules with the magnetite particles inside are formed.

The following set of samples was prepared by mechanical mixing of solutions of the corresponding polymers with magnetite suspension.

2XS – 0.3 % solution of chitosan was blended with 100 μl of magnetite suspension;

2AS – 0.3 % solution of sodium alginate was mixed with 100 μl of magnetite suspension.

The following solutions for the spray-method were obtained by mixing:

3XS – 0.3 % solution of chitosan was blended with 100 μl of magnetite suspension;

3AS – 0.3 % solution of sodium alginate was mixed with 100 μl of magnetite suspension.

Then, the obtained solutions were sprayed by spray-method onto a copper mesh with a carbon film for the transmission electron microscopy (TEM). Facility for the spray-method consists of the compressor and sprayer. Varying experimentally diameter of the sprayer nozzle, we have matched the conditions for spraying of nano-dispersed particles.

X-ray investigation of magnetic composites was performed on the automated diffractometer DRON-3 (scientific-manufacturing company "Burevestnik", S.-Petersburg) in CuK_α-radiation (wavelength 0.154 nm) under conditions of the Bragg-Brentano focusing θ-2θ (2θ is the Bragg angle). Current and voltage of the X-ray tube were equal to 20 mA and 40 kV, respectively. Processing of the results was carried out using the software package DifWin-1 (LLC "Etalon PTTs"). Identification of the crystalline phases was done by the JCPDS file (Joint Committee on Powder Diffraction Standards).

Average crystallite sizes were found by the Scherrer formula [20]. Calculation of the crystal lattice parameter was realized by the extrapolation function method which allows to extrapolate the lattice parameter to the angle of $\theta = 90°$ (the error in determination of the interplanar spacings and lattice parameter tends to zero). Nelson-Reilly function was used as extrapolation function [21].

Electron microscopic and electron diffraction studies were performed on the transmission electron microscope PEM-125K (public Corp. "SELMI", Sumy). The operating conditions are the following: accelerating voltage 90 kV, beam current 100 μA, aperture diaphragm size 0.1 mm (in the electron diffraction mode). Investigations of the samples using TEM were carried out after their preliminary preparation on ultrasonic device UZDN-A (public Corp. "SELMI", Sumy). Eppendorf microtube with the solution of magnetic nanoparticles was placed into an ultrasonic cup (radiator) with distilled water for 10 min with the specific radiation power of 15-20 W/cm^2 and radiation frequency of 22 kHz. Then, dispersed solution was applied to the ultrasonic radiator with a flat tip and sprayed on a thin carbon film of the thickness 10-20 nm located on a special copper mesh for TEM. Measurements of the linear sizes of magnetic nanoparticles were carried out using VideoTesT program (LLC "VideoTesT", S.-Petersburg) [22]. Interpretation of the electron diffraction patterns was performed using JCPDS data.

3. RESULTS AND DISCUSSION

X-ray diffraction studies were carried out for both the initial (alginate and chitosan films) and final products (the same films with addition of magnetite). On the spectra of the initial samples (Fig. 1a, c) one observes the pronounced halo near $2\theta \sim 20^o$ and, probably, 10^o that is typical for the given materials [23, 24].

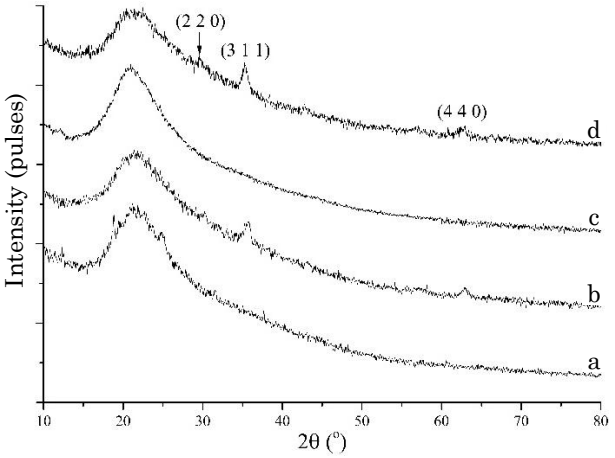

Fig. 1 – Diffraction patterns of the samples obtained by mixing (2AS, 2XS): sodium alginate (a); alginate-magnetite (2AS) (b); chitosan (c); chitosan-magnetite (2XS) (d)

Phase analysis of the final products (Fig. 1b, d) has shown the presence of the initial materials (alginate and chitosan) as well as magnetite (JCPDS 75-449). The diffraction pattern and average crystallite sizes point to the similar crystallinity of Fe_3O_4 in both final samples, slightly better in the case of alginate (Fig. 1b).

Presence of chitosan leads to more significant distortions of the magnetite crystal lattice, in particular, to its contraction, that is confirmed by the calculations of the lattice parameter by the Nelson-Reilly method (Table 1).

Using TEM, we have obtained the micrographs of the agglomerates of magnetic composite nanoparticles with different magnification, on which one can clearly see the shape, size of both agglomerates and separate particles as well as the presence of a polymer cover (Fig. 2).

Micro-electron diffraction patterns of the samples 1AS and 1XS were obtained (Fig. 3). Presence of point reflexes in the electron diffraction pattern rings implies that diffraction pattern is formed on agglomerates of particles of the given sample.

Table 1 – Structural parameters of the polymer-magnetite samples obtained by mixing

Sample	Average crystallite size by Scherrer, nm			Lattice parameter, nm
	(2 2 0)	(3 1 1)	(4 4 0)	
2AS	23.2	8.9	10	0.835
2XS	15	10.7	10.2	0.8247

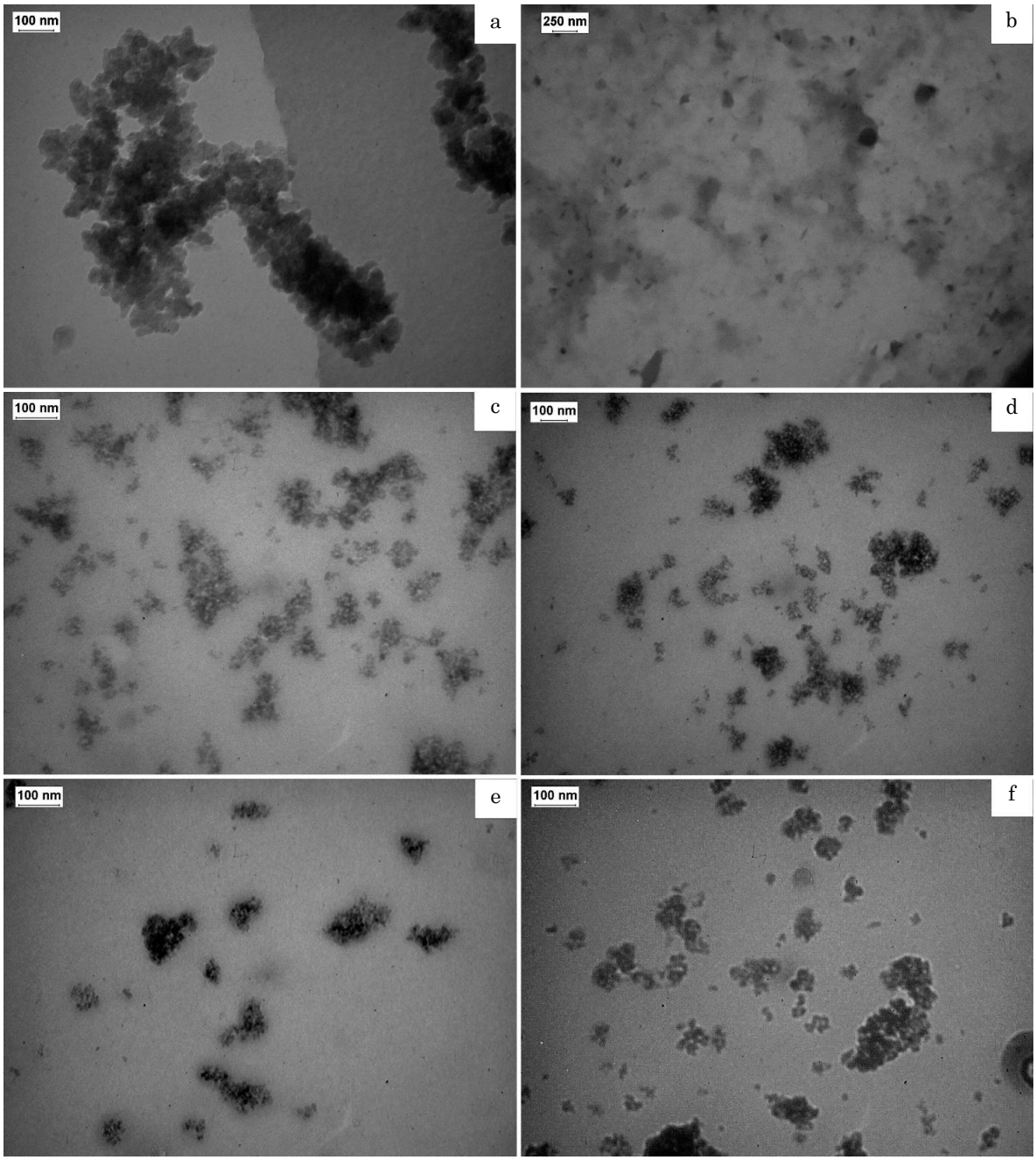

Fig. 2 – Electron microscopic images of the particles of magnetic nanocomposites: 2XS (a), 2AS (b), 1XS (c), 1AS (d), 3XS (e), 3AS (f)

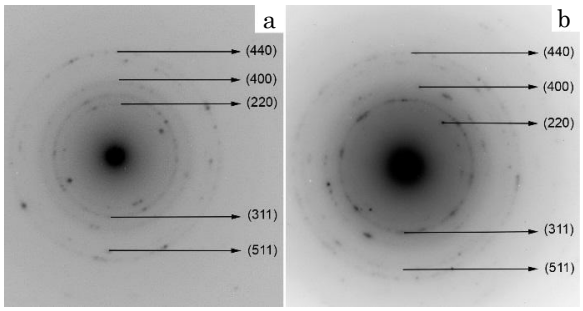

Fig. 3 – Micro-electron diffraction patterns of the samples of magnetic nanocomposites: 2XS (a), 2AS (b)

Miller indices which correspond to the reflexes of magnetite Fe_3O_4 (JCPDS 19-629) are indicated on the micro-electron diffraction patterns. Polymer components, such as chitosan and alginate are amorphous, therefore, they are absent on the diffraction pattern.

Using electron microscopic images of the magnetic nanocomposite particles, the histograms of the particle size distribution (Fig. 4) were plotted. It is seen from the histograms that samples 1AS, 1XS and 3AS, 3XS have the smallest particle sizes and also have a small spread in their values (sample 1XS – 8-18 nm; 1AS – 4-12 nm, 3XS – 5-17 nm, 3AS – 8-22 nm). The samples obtained by mixing (2AS, 2XS) have larger values of the particle sizes (2XS – 20-34 nm, 2AS – 50-100 nm).

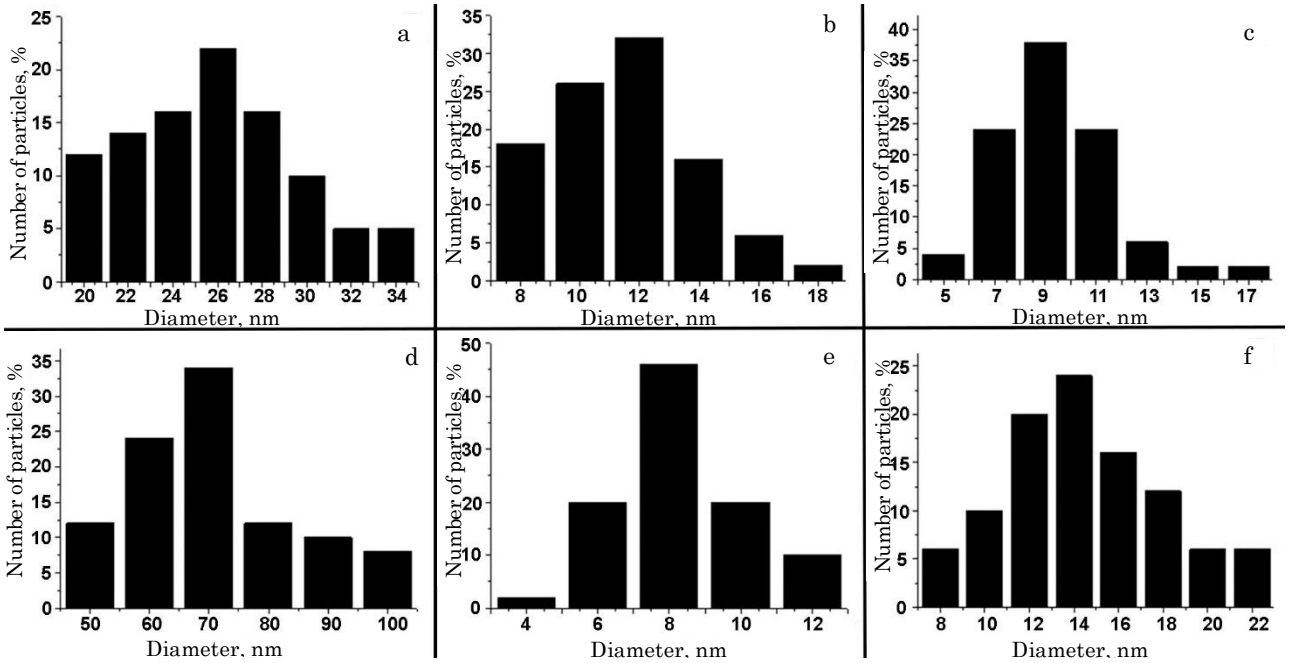

Fig. 4 – Particle size distribution of the samples of magnetic nanocomposites: 2XS (a), 1XS (b), 3XS (c), 2AS (d), 1AS (e), 3AS (f)

4. CONCLUSIONS

Comparison of the ways of obtaining magnetite nanoparticles in a polymer cover of alginate or chitosan has shown that structural features of the samples obtained by spray-method and synthesis have substantial advantages over those of the samples obtained at simple mixing of a polymer solution with magnetite particles. Size of the magnetite particles in a polymer cover obtained by synthesis and spray-method are on average equal to 4-22 nm, while during mixing – 50-100 nm. Calculation of the average crystallite sizes shows insignificant differences in the crystallinity of Fe_3O_4 in the samples obtained by mixing, which is more expressed than in the case of alginate. The presence of chitosan leads to larger distortion of the magnetite crystal lattice, in particular, to its contraction that is seen from the calculated parameters of the crystal lattice.

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